

# Ferromagnetism in III-V and II-VI semiconductor structures

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The current status of research on the carrier-mediated ferromagnetism in tetrahedrally coordinated semiconductors is briefly reviewed. The experimental results for III-V semiconductors, where Mn atoms introduce both spins and holes, are compared to the case of II-VI compounds, in which the ferromagnetism has been observed for the modulation-doped p-type  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}/\text{Cd}_{1-y-z}\text{Mg}_y\text{Zn}_z\text{Te:N}$  heterostructures, and more recently, in  $\text{Zn}_{1-x}\text{Mn}_x\text{Te:N}$  epilayers. On the theoretical side, a model is presented, which takes into account: (i) strong spin-orbit and  $kp$  couplings in the valence band; (ii) the effect of confinement and strain upon the hole density-of-states and response function, and (iii) the influence of disorder and carrier-carrier interactions, particularly near the metal-to-insulator transition. A comparison between experimental and theoretical results demonstrates that the model can describe the magnetic circular dichroism, the values of  $T_C$  observed in the studied systems as well as explain the directions of the easy axis and the magnitudes of the corresponding anisotropy fields as a function of confinement and biaxial strain. Various suggestions concerning design of novel ferromagnetic semiconductor systems are described.

## I. INTRODUCTION

Because of complementary properties of semiconductor and ferromagnetic material systems, a growing effort is directed toward studies of semiconductor-magnetic nanostructures. Applications in sensors and memories [1] as well as for computing using electron spins can be envisaged [2]. The hybrid nanostructures, in which both electric and magnetic field are spatially modulated, are usually fabricated by patterning of a ferromagnetic metal on the top of a semiconductor [3] or by incorporation of ferromagnetic clusters into a semiconductor matrix [4]. In such devices, the stray fields can control charge and spin dynamics in the semiconductor. At the same time, spin-polarized electrons from the metal could be injected into the semiconductor. The efficiency of such a process appears, however, to be prohibitively low [5-7].

Already the early studies of Cr spinels [8] and rock-salt Eu [9,10] and Mn-based [11] chalcogenides led to the observation of a number of outstanding phenomena associated with the interplay between ferromagnetic cooperative phenomena and semiconducting properties. The discovery of ferromagnetism in zinc-blende III-V [12,13] and II-VI [14,15] Mn-based compounds allows one to explore physics of previously not available combinations of quantum structures and magnetism in semiconductors. For instance, a possibility of changing the magnetic phase by light in (In,Mn)As/(Al,Ga)Sb [16] and (Cd,Mn)Te/(Cd,Zn,Mg)Te [14] heterostructures was put into the evidence. The injection of spin-polarized carriers from (Ga,Mn)As to a (In,Ga)As quantum well in the absence of an external magnetic field was demonstrated, too [17]. It is then important to understand the ferromagnetism in these semiconductors, and to ask whether the Curie temperatures  $T_C$  can be raised to above 300 K from the present 110 K observed for  $\text{Ga}_{0.947}\text{Mn}_{0.053}\text{As}$  [13,18]. In this paper, we outline briefly the main ingredients of a model put recently forward to describe quantitatively the hole-mediated ferromagnetism in tetrahedrally coordinated semiconductors [19]. We also list a number of counterintuitive experimental findings, which are explained by the model. Finally, we present the relevant chemical trends and discuss various suggestions concerning the design of novel ferromagnetic semiconductor systems. The recent comprehensive reviews present many other aspects of III-V [20], II-VI [21] as well as of IV-VI [11] magnetic semiconductors, which are not discussed here.

## II. ORIGIN OF FERROMAGNETISM

Since we aim at quantitative description of experimental findings, the proposed theoretical approach [19] makes use of empirical facts and parameters wherever possible. In this section, we discuss those effects, which are regarded as crucial in determining the magnitude of fer-

romagnetic couplings in p-type magnetic semiconductors [19].

### A Charge and spin state of Mn ions

We consider tetrahedrally coordinated semiconductors, in which the magnetic ion Mn occupies the cation sublattice, as found by extended x-ray absorption fine structure (EXAFS) studies in the case of  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  [22] and  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  [23]. The Mn provides a localized spin and, in the case of III-V semiconductors, acts as an acceptor. These Mn acceptors compensate the deep antisite donors commonly present in GaAs grown by low-temperature molecular beam epitaxy, and produce a p-type conduction with metallic resistance for the Mn concentration  $x$  in the range  $0.04 \leq x \leq 0.06$  [18,24-26]. According to optical studies, Mn in GaAs forms an acceptor center characterized by a moderate binding energy [27]  $E_a = 110$  meV, and a small magnitude of the energy difference between the triplet and singlet state of the bound hole [27,28]  $\Delta\epsilon = 8 \pm 3$  meV. This small value demonstrates that the hole introduced by the divalent Mn in GaAs does not reside on the d shell or forms a Zhang-Rice-like singlet [29,30], but occupies an effective mass Bohr orbit [19,31]. Thus, due to a large intra-site correlation energy  $U$ ,  $(\text{Ga},\text{Mn})\text{As}$  can be classified as a charge-transfer insulator, a conclusion consistent with photoemission spectroscopy [32,33]. At the same time, the p-d hybridization results in a spin-dependent coupling between the holes and the Mn ions,  $H_{pd} = -\beta N_o \mathbf{s} \cdot \mathbf{S}$ . Here  $\beta$  is the p-d exchange integral and  $N_o$  is the concentration of the cation sites. The analysis of both photoemission data [32,33] and magnitude of  $\Delta\epsilon$  [31] leads to the exchange energy  $\beta N_o \approx -1$  eV. Similar values of  $\beta N_o$  are observed in II-VI diluted magnetic semiconductors with comparable lattice constants [34]. This confirms Harrison's suggestion that the hybridization matrix elements depend primarily on the intra-atomic distance [35]. According to the model in question, the magnetic electrons remain localized at the magnetic ion, so that they do not contribute to charge transport. This precludes Zener's double exchange [36] as the mechanism leading to ferromagnetic correlation between the distant Mn spins. At the same time, for some combinations of transition metals and hosts, the "chemical" attractive potential introduced by the magnetic ion can be strong enough to bind the hole on the local orbit [29,30]. In an intermediate regime, the probability of finding the hole around the magnetic ion is enhanced, which result in the apparent increase of  $|\beta N_o|$  with decreasing  $x$  [30].

In addition to the carrier-spin interaction, the p-d hybridization leads to the superexchange, a short-range antiferromagnetic coupling between the Mn spins. In order to take the influence of this interaction into account, it is convenient to parameterize the dependence of magnetization on the magnetic field in the absence of the carriers,

$M_o(H)$ , by the Brillouin function, in which two empirical parameters, the effective spin concentration  $x_{eff}N_o < xN_o$  and temperature  $T_{eff} > T$ , take the presence of the superexchange interactions into account [34,37,38]. The dependencies  $x_{eff}(x)$  and  $T_{AF}(x) \equiv T_{eff}(x) - T$  are known [37,38] for (Zn,Mn)Te, while  $x \approx x_{eff}$  and  $T_{AF} \approx 0$  for (Ga,Mn)As, as explained below.

## B Electronic states near metal-insulator transition

Because of ionized impurity and magnetic scattering, the effective mass holes introduced by Mn in III-V compounds or by acceptors such as N or P in the case of II-VI DMS, are at the localization boundary. It is, therefore, important to discuss the effect of localization on the onset of ferromagnetism. The two-fluid model [39] constitutes the established description of electronic states in the vicinity of the Anderson-Mott metal-insulator transition (MIT) in doped semiconductors. According to that model, the conversion of itinerant electrons into singly occupied impurity states with increasing disorder occurs gradually, and begins already on the metal side of the MIT. This leads to a disorder-driven static phase separation into two types of regions: one populated by electrons in extended states, and another containing singly occupied impurity-like states. The latter controls the magnetic response of doped non-magnetic semiconductors [39] and gives rise to the presence of BMPs on both sides of the MIT in magnetic semiconductors [34,40,41]. Actually, the formation of BMPs shifts the MIT towards the higher carrier concentrations [34,40,41]. On crossing the MIT, the extended states become localized. However, according to the scaling theory of the MIT, their localization radius  $\xi$  decreases rather gradually from infinity at the MIT towards the Bohr radius deep in the insulator phase, so that on a length scale smaller than  $\xi$  the wave function retains an extended character. Such weakly localized states are thought to determine the static longitudinal and Hall conductivities of doped semiconductors.

The central suggestion of the recent model [19] is that the holes in the extended or weakly localized states mediate the long-range interactions between the localized spins on both sides of the MIT in the III-V and II-VI magnetic semiconductors. As will be discussed below,  $T_C$  is proportional to the spin susceptibility of the carrier gas  $\chi_s$  which, in turn, is proportional to the thermodynamic spin density-of-states  $\rho_s$ . Like other thermodynamic quantities,  $\rho_s$  does not exhibit any critical behavior at the MIT. The quantitative renormalization of  $\rho_s$  by disorder will depend on its actual form, for instance, on the degree of compensation. The enhancement of  $\rho_s$  by the carrier-carrier interactions can be described by the Fermi-liquid parameter  $A_F$ ,  $\rho_s \rightarrow A_F \rho_s$ . The value of  $A_F = 1.2$ , as evaluated [42] by the local-spin-density approximation for the relevant hole concentrations, has been adopted for the computations.

The participation of the same set of holes in both charge transport and the ferromagnetic interactions is shown, in (Ga,Mn)As [24] and in (Zn,Mn)Te [22], by the agreement between the temperature and field dependences of the magnetization deduced from the extraordinary Hall effect,  $M_H$ , and from direct magnetization measurements,  $M_D$ , particularly in the vicinity of  $T_C$ . However, below  $T_C$  and in the magnetic fields greater than the coercive force, while  $M_H$  saturates (as in standard ferromagnets),  $M_D$  continues to rise with the magnetic field [24,43]. This increase is assigned to the BMPs, which interact weakly with the ferromagnetic liquid. To gain the Coulomb energy, the BMPs are preferentially formed around close pairs of ionized acceptors. In the case of p-(Ga,Mn)As this leads to a local ferromagnetic alignment of neighbor Mn d<sup>5</sup> negative ions [44], so that  $x \approx x_{eff}$  and  $T_{AF} \approx 0$ . By contrast, BMPs in p-(Zn,Mn)Te are not preferentially formed around Mn pairs and encompass more Mn spins for a given  $x$ , as the small binding energy [45]  $E_a = 54$  meV corresponds to a relatively large localization radius. The presence of a competition between the ferromagnetic and antiferromagnetic interactions in II-VI compounds, and its absence in III-V materials, constitutes the important difference between those two families of magnetic semiconductors.

## C The structure of the valence band

The meaningful model of the hole-mediated ferromagnetism has to take into account the complex nature of the valence band in semiconductors resulting from  $kp$  and spin-orbit interactions. Therefore, the hole dispersion and wave functions are computed by diagonalizing the 6x6 Kohn-Luttinger matrix [46] together with the recalculated p-d exchange contribution [47]. The model is developed for zinc-blende and wurzite semiconductors, allows for warping, quantizing magnetic fields, strain, and arbitrary orientations of  $\mathbf{M}$ . Because of the spin-orbit interaction, the exchange splitting of the valence band depends on the relative orientation of the magnetization and the hole wave vector. This mixing of orbital and spin degrees of freedom [48] accounts for substantial differences between the effects of the exchange interaction upon properties of the electron and hole liquids. The tabulated values of the effective-mass constants [49-52] are taken as input parameters. According to interband magnetoptics [37] and photoemission studies [32]  $\beta N_o = -1.1 \pm 0.1$  and  $-1.2 \pm 0.2$  eV for (Zn,Mn)Te and (Ga,Mn)As, respectively.

## D Zener model of carrier-mediated ferromagnetism

Zener [53] first proposed the model of ferromagnetism driven by the exchange interaction between carriers and

localized spins. However, this model was later abandoned, as neither the itinerant character of the magnetic electrons nor the quantum (Friedel) oscillations of the electron spin-polarization around the localized spins were taken into account, both of these are now established to be critical ingredients for the theory of magnetic metals. In particular, a resulting competition between ferromagnetic and antiferromagnetic interactions leads rather to a spin-glass than to a ferromagnetic ground state. In the case of semiconductors, however, the mean distance between the carriers is usually much greater than that between the spins. Under such conditions, the exchange interaction mediated by the carriers is ferromagnetic for most of the spin pairs, which reduces the tendency towards spin-glass freezing. Actually, for a random distribution of the localized spins, the mean-field value of the Curie temperature  $T_C$  deduced from the Zener model is equal to that obtained from the Ruderman, Kittel, Kasuya, and Yosida (RKKY) approach, in which the presence of the Friedel oscillations is explicitly taken into account [54,55].

The starting point of the model is the determination how the Ginzburg-Landau free-energy functional  $F$  depends on the magnetization  $M$  of the localized spins. As mentioned above, the hole contribution to  $F$ ,  $F_c[M]$  is computed by diagonalizing the 6x6 Kohn-Luttinger matrix together with the p-d exchange contribution, and by the subsequent computation of the partition function  $Z$ . This model takes the effects of the spin-orbit interaction into account, a task difficult technically within the RKKY approach, as the spin-orbit coupling leads to non-scalar terms in the spin-spin Hamiltonian. Moreover, the indirect exchange associated with the virtual spin excitations between the valence bands, the Bloembergen-Rowland mechanisms [34], is automatically included.

The remaining part of the free energy functional, that of the localized spins, is given by

$$F_S[M] = \int_0^M dM_o H(M_o), \quad (1)$$

where  $H(M_o)$  is the inverse function of the experimental dependence of the magnetization on the magnetic field  $H$  in the absence of the carriers. By minimizing  $F = F_c[M] + F_S[M]$  with respect to  $M$  at given  $T$ ,  $H$ , and hole concentration  $p$ , one obtains  $M(T, H)$  within the mean-field approximation, an approach that is quantitatively valid for long-range exchange interactions.

### E Curie temperature

As described above,  $T_C$  can be computed by minimizing the free energy, and without referring to the explicit form of the carrier periodic wave functions  $u_{i\mathbf{k}}$ . Since near  $T_C$  the relevant magnetization  $M$  becomes small, the carrier free energy, and thus  $T_C$ , can also be determined from the linear response theory. The resulting  $T_C$

assumes the general form

$$T_C = x_{eff} N_o S(S+1) \beta^2 A_F \rho_s(0, T_C) / 12k_B - T_{AF}. \quad (2)$$

In the absence of disorder

$$\rho_s(\mathbf{q}, T) = 8 \sum_{i\mathbf{j}\mathbf{k}} \frac{|\langle u_{i\mathbf{k}} | s_z | u_{j\mathbf{k}+\mathbf{q}} \rangle|^2 f_i(\mathbf{k}) [1 - f_j(\mathbf{k} + \mathbf{q})]}{[E_j(\mathbf{k} + \mathbf{q}) - E_i(\mathbf{k})]}, \quad (3)$$

where  $z$  is the direction of magnetization and  $f_i(\mathbf{k})$  is the Fermi-Dirac distribution function for the  $i$ -th valence band subband. It is seen that for spatially uniform magnetization (the ferromagnetic case), only the terms corresponding to  $q = 0$  (i.e., the diagonal terms) determine  $T_C$ . For the strongly degenerate carrier gas as well as neglecting the spin-orbit interaction,  $\rho_s$  is equal to the total density-of-states  $\rho$  for intra-band charge excitations, where  $\rho = m_{DOS}^* k_F / \pi^2 \hbar^2$ .

Equation (2) for  $T_C$  with  $\rho_s = \rho$  has already been derived by a number of equivalent methods [34,42,54,55]. It is straightforward to generalize the model for the case of the carriers confined to the  $d$ -dimensional space [14,54,55]. The tendency towards the formation of spin-density waves in low-dimensional systems [55] as well as possible spatial correlation in the distribution of the magnetic ions can also be taken into account. The mean-field value of the critical temperature  $T_{\mathbf{q}}$ , at which the system undergoes the transition to a spatially modulated state characterized by the wave vector  $\mathbf{q}$ , is given by the solution of the equation,

$$\beta^2 A_F(\mathbf{q}, T_{\mathbf{q}}) \rho_s(\mathbf{q}, T_{\mathbf{q}}) \int d\zeta \chi_o(\mathbf{q}, T_{\mathbf{q}}, \zeta) |\phi_o(\zeta)|^4 = 4g^2 \mu_B^2. \quad (4)$$

Here  $\mathbf{q}$  spans the  $d$ -dimensional space,  $\phi_o(\zeta)$  is the envelope function of the carriers confined by a  $(3 - d)$ -dimensional potential well  $V(\zeta)$ ;  $g$  and  $\chi_o$  denote the Landé factor and the  $\mathbf{q}$ -dependent magnetic susceptibility of the magnetic ions in the absence of the carriers, respectively. Within the MFA, such magnetization shape and direction will occur in the ordered phase, for which the corresponding  $T_{\mathbf{q}}$  attains the highest value.

## III. COMPARISON OF THE MODEL TO SELECTED EXPERIMENTAL RESULTS

### A Magnetic circular dichroism in (Ga,Mn)As

In the case of II-VI DMS, detail information on the exchange-induced spin-splitting of the bands, and thus on the coupling between the effective mass electrons and the localized spins has been obtained from magneto-optical studies [34,47]. A similar work on (Ga,Mn)As [43,56,57] led to a number of surprises. The most striking was the opposite order of the absorption edges corresponding to

the two circular photon polarizations in (Ga,Mn)As comparing to II-VI materials. This behavior of circular magnetic dichroism (MCD) suggested the opposite order of the exchange-split spin subbands, and thus a different origin of the sp-d interaction in these two families of DMS. A new light on the issue was shed by studies of photoluminescence (PL) and its excitation spectra (PLE) in p-type (Cd,Mn)Te quantum wells [14]. As shown schematically in Fig. 1, the reversal of the order of PLE edges corresponding to the two circular polarizations results from the Moss-Burstein effect, that is from the shifts of the absorption edges associated with the empty portion of the valence subbands in the p-type material. This model was subsequently applied to interpret qualitatively the magnetoabsorption data for metallic (Ga,Mn)As [57]. Surprisingly, however, the anomalous sign of the MCD was present also in non-metallic (Ga,Mn)As, in which EPR signal from occupied Mn acceptors was seen [57]. It has, therefore, been suggested that the exchange interaction between photo- and bound-holes is responsible for the anomalous sign of the MCD in those cases [57]. The presence of such a strong exchange mechanism is rather puzzling, and it should be seen in non-magnetic p-type semiconductors. At the same time, according to our two-fluid model, the co-existence of strongly and weakly localized holes is actually expected on the both sides of the MIT. Since the Moss-Burstein effect operates for interband optical transitions involving weakly localized states, it leads to the sign reversal of the MCD, also on the insulating side of the MIT.

Another striking property of the MCD is a different temperature dependence of the normalized MCD at low and high photon energies in ferromagnetic (Ga,Mn)As [43]. This observation was taken as an evidence for the presence of two spectrally distinct contributions to optical absorption [43]. A quantitative computation of MCD spectra has recently been undertaken [58]. The theoretical results demonstrate that because of the Moss-Burstein effect, the magnetization-induced splitting of the bands leads to a large energy difference between the positions of the absorption edges corresponding to the two opposite circular polarizations. This causes an unusual dependence of the low-energy onset of MCD on magnetization, and thus on temperature. These considerations lead to a quantitative agreement with the experimental findings, provided that the actual hole dispersion and wave functions are taken for the computation of MCD.

## B Curie temperature in (Ga,Mn)As, (Zn,Mn)Te and (Cd,Mn)Te quantum well

The most interesting property of  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  epilayers is the large magnitude of  $T_C$ , of the order of 100 K for the Mn concentration  $x$  as low as 5% [13,18]. Because of this high  $T_C$ , the spin-dependent extraordinary contribution to the Hall resistance  $R_H$  persists up to 300 K, mak-

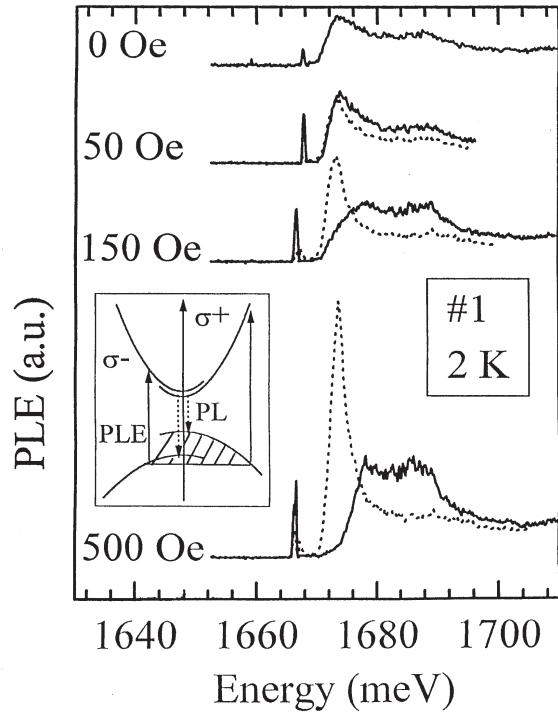


FIG. 1: Photoluminescence excitation spectra (PLE), that is the photoluminescence (PL) intensity as a function of the excitation photon energy intensity, for  $\sigma^+$  (solid lines) and  $\sigma^-$  (dotted lines) circular polarizations at selected values of the magnetic field in a modulation-doped p-type quantum well of  $\text{Cd}_{0.976}\text{Mn}_{0.024}\text{Te}$  at 2 K. The photoluminescence was collected in  $\sigma^+$  polarization at energies marked by the narrowest features. The sharp maximum and step-like form correspond to quasi-free exciton and transitions starting at the Fermi level, respectively. Note reverse ordering of transition energies at  $\sigma^+$  and  $\sigma^-$  for PL and PLE (the latter is equivalent to optical absorption). The band arrangement at 150 Oe is sketched in the inset (after [14]).

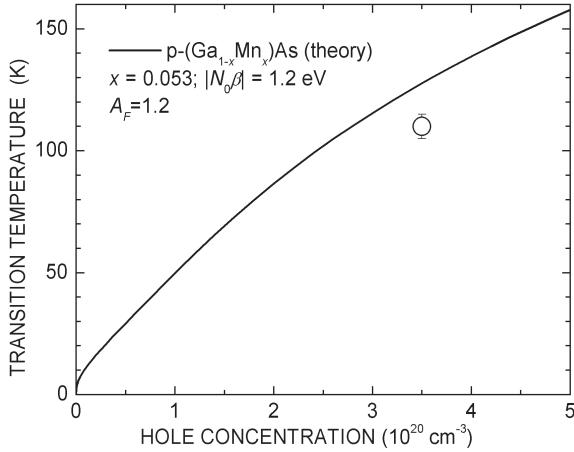


FIG. 2: Calculated ferromagnetic transition temperature as a function of hole concentration for  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  with  $x = 0.053$  [19]. The open circle indicates the experimental result for  $p = 3.5 \times 10^{20} \text{ cm}^{-3}$  (after [18]).

ing an accurate determination of the hole density difficult [18, 24–26]. However, the recent measurement [59] of  $R_H$  up to 27 T and at 50 mK yielded an unambiguous value of  $p = 3.5 \times 10^{20} \text{ cm}^{-3}$  for a metallic  $\text{Ga}_{0.947}\text{Mn}_{0.053}\text{As}$  sample, in which  $T_C = 110 \text{ K}$  is observed [18]. As shown in Fig. 2, the present model explains, with no adjustable parameters, such a high value of  $T_C$ .

The studied epilayers of  $(\text{Zn},\text{Mn})\text{Te:N}$  [15] were on the insulating side of the metal-insulator transition (MIT), as the bound magnetic polaron (BMP) formation enhances localization. Nevertheless, if the concentration of acceptors was sufficiently high, the ferromagnetic Curie-Weiss temperatures  $T_{CW}$  were observed as well as magnetic hysteresis were detected below  $T_C \approx T_{CW}$  [15]. At the same time, the values of  $T_C$  were much lower than those characterizing  $(\text{Ga},\text{Mn})\text{As}$ . However, a comparison of the experimental and calculated values of  $T_C$  for  $(\text{Zn},\text{Mn})\text{Te}$  as a function of  $x$  and  $p$  (Fig. 3) demonstrates that the present model is capable to explain the magnitude of  $T_C$  except for the samples with the smallest  $x$ . In the latter,  $p/xN_o$  is as large as 0.6, so that precursor effects of Friedel oscillations and Kondo correlation are expected at low temperatures [54].

Two effects appear to account for the greater  $T_C$  values in  $p-(\text{Ga},\text{Mn})\text{As}$  than in  $p-(\text{Zn},\text{Mn})\text{Te}$  at given  $p$  and  $x$ . First is the smaller magnitude of the spin-orbit splitting between the  $\Gamma_8$  and  $\Gamma_7$  bands in arsenides,  $\Delta_o = 0.34 \text{ eV}$ , in comparison to that of tellurides,  $\Delta_o = 0.91 \text{ eV}$ . Once the Fermi energy  $E_F$  approaches the  $\Gamma_7$  band, the density-of-states effective mass increases, and the reduction of the carrier spin susceptibility by the spin-orbit interaction is diminished. The computed value of  $T_C$  for  $p = 3 \times 10^{20} \text{ cm}^{-3}$  is greater by a factor of four in  $(\text{Ga},\text{Mn})\text{As}$  than that evaluated in the limit  $\Delta_o \gg E_F$ . The other difference between the two materials is the de-

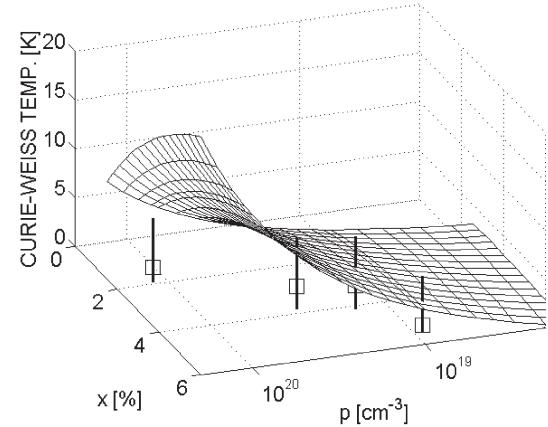


FIG. 3: Curie-Weiss temperature in  $\text{Zn}_{1-x}\text{Mn}_x\text{Te:N}$  for various Mn contents  $x$  and hole concentrations  $p$ , determined from the temperature dependence of the magnetic susceptibility. Experimental values are marked by squares [15] while theoretical predictions by the mesh (after [19]).

structive effect of antiferromagnetic interactions, which operate in II-VI compounds but are of minor importance in III-V materials, as explained in Sec. 2.

The model discussed above describes also the magnitude of  $T_C$  and its dependence on  $x$  in modulation-doped quantum wells of  $p-(\text{Cd},\text{Mn})\text{Te}$ , if  $A_F = 2$  is assumed [60], an expected value for the relevant densities of the two-dimensional hole liquid. A good description of  $T_C(p)$  is also obtained, provided that disorder broadening of the density-of-states at low  $p$  is taken into account [60]. Whether the ground state corresponds to uniform magnetization or rather to a spin-density wave is under study now.

### C Effects of strain

Already early studies of a ferromagnetic phase in  $(\text{Ga},\text{Mn})\text{As}$  epilayers demonstrated the existence of substantial magnetic anisotropy [61]. Magnetic anisotropy is usually associated with the interaction between spin and orbital degrees of freedom of the magnetic electrons. According to the model in question, these electrons are in the  $d^5$  configuration. For such a case the orbital momentum  $L = 0$ , so that no effects stemming from the spin-orbit coupling could be expected. To reconcile the model and the experimental observations, we note that the interaction between the localized spins is mediated by the holes, characterized by a non-zero orbital momentum. An important aspect of the present model is that it does take into account the anisotropy of the carrier-mediated exchange interaction associated with the spin-orbit coupling in the host material, an effect difficult to include

within the standard approach to the RKKY interaction.

The computed effect of the cubic anisotropy on  $T_C$  has been found to be small; differences between  $T_C$  values calculated for various orientations of magnetization in respect to crystallographic axes are below 0.1 K in (Ga,Mn)As [58]. The corresponding differences are, however, greater in the presence of epitaxial strain; of the order of 1 K for 1% biaxial strain in the (001) plane. Thus, such a strain can control the orientation of the easy axis. According to the computation for the relevant hole concentrations, the easy axis is in the plane for the case of unstrained or compressively strained films but under tensile strain the easy axis takes the [001] direction. These expectations [58] are corroborated by the experimental study, in which appropriate substrates allowed to control the direction of strain [61]. It is worth noting that similarly to strain, also confinement of the holes affects the magnetic anisotropy in accord with the theoretical model, the easy axis is oriented along the growth direction in the ferromagnetic p-(Cd,Mn)Te quantum wells [14,60].

#### IV. OTHER PERSPECTIVE MATERIALS

In view of the general agreement between experiment and theory for  $T_C$  and the magnetic anisotropy, it is tempting to extend the model for material systems that might be suitable for fabrication of novel ferromagnetic semiconductors. For instance, the model suggests immediately that  $T_C$  values above 300 K could be achieved in  $\text{Ga}_{0.9}\text{Mn}_{0.1}\text{As}$ , if such a large value of  $x$  would be accompanied by a corresponding increase of the hole concentration. Figure 4 presents the values of  $T_C$  computed for various tetrahedrally coordinated semiconductors containing 5% of Mn and  $3.5 \times 10^{20}$  holes per  $\text{cm}^3$  [19]. In addition to adopting the tabulated values of  $\gamma_i$  and  $\Delta_o$  [49-52] the same value of  $\beta = \beta[(\text{Ga,Mn})\text{As}]$  for all group IV and III-V compounds was assumed, which results in an increase of  $|\beta N_o| \sim a_o^{-3}$ , where  $a_o$  is the lattice constant, a trend known to be obeyed within the II-VI family of magnetic semiconductors [34]. By extending the model for wurtzite semiconductors,  $T_C$  values for parameters of  $\text{ZnO}$  [62] (Fig. 3) and for wurtzite GaN (not shown) were evaluated. For the employed parameters [63] the magnitude of  $T_C$  for the cubic GaN (Fig. 4) is by 6% greater than that computed for the wurtzite structure.

The data (Fig. 4) demonstrate that there is much room for a further increase of  $T_C$  in p-type magnetic semiconductors. In particular, a general tendency for greater  $T_C$  values in the case of lighter elements stems from the corresponding increase in p-d hybridization and reduction of spin-orbit coupling. It can be expected that this tendency is not altered by the uncertainties in the values of the relevant parameters. Important issues of solubility limits and self-compensation as well as of the transition to a strong-coupling case with decreasing  $a_o$  [30] need to be addressed experimentally. We note in this context that

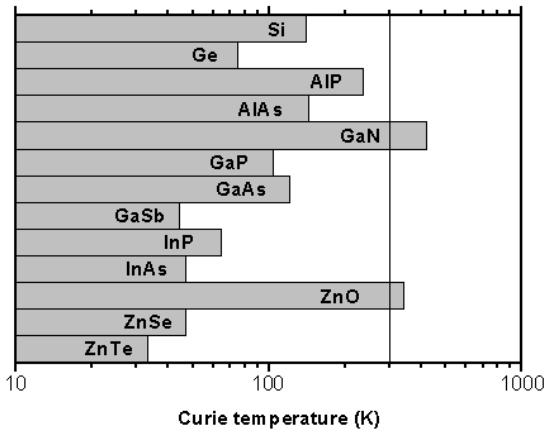


FIG. 4: Computed values of the Curie temperature  $T_C$  for various p-type semiconductors containing 5% of Mn and  $3.5 \times 10^{20}$  holes per  $\text{cm}^3$  (after [19]).

since, in general, III-V compounds can easier be doped by impurities that are electrically active, whereas II-VI materials by transition metals, a suggestion has been put forward to grow magnetic III-V/II-VI short period superlattice [64].

Finally, we address the important question about the feasibility of synthesizing n-type or intrinsic ferromagnetic semiconductors. A work on  $(\text{Zn,Mn})\text{O}: \text{Al}$  [65] is relevant in this context. One should not forget, however, about the existence of, e.g., europium chalcogenides and chromium spinels, whose ferromagnetism is not driven by free carriers. Actually, a theoretical suggestion has been made [66] that superexchange in Cr-based II-VI compounds can lead to a ferromagnetic order. Desired material properties, such as divergent magnetic susceptibility and spontaneous magnetization, can also be achieved in the case of a strong antiferromagnetic super-exchange interaction. The idea here [67] is to synthesize a ferrimagnetic system that would consist of antiferromagnetically coupled alternating layers containing different magnetic cations, e.g., Mn and Co.

The above list of possibilities is by no means exhausting. With no doubt we will witness many unforeseen developments in the field of ferromagnetic semiconductors in the near future.

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